

## DESCRIPTION

### METHOD FOR CONNECTING ELECTRONIC PARTS

#### 5 TECHNICAL FIELD

The present invention relates to a method for connecting electronic parts, and particularly to a lead-free solder and a plating coat to be connected to the solder.

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#### BACKGROUND ART

Along with the recent development of small-sized and highly dense portable communication devices, personal computers, audio devices, and the like, small-sized and  
15 light weight electronic parts have been desired. The development of small-sized electronic parts has made the area of connecting terminals, such as terminal electrodes, small. Therefore, inferior connection tends to be caused, and a need has arisen to increase connection reliability.

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As to connection reliability, it is desirable to improve the wettability of an electrode to a solder, and adhesive strength between a solder and an electrode. Conventionally, there has been a tendency to use electroless Ni/Au plating for the surface treatment of the  
25 electrode, to improve wettability to a solder. This

electroless Ni/Au plating is accomplished by performing electroless Ni plating with phosphorous on an electrode terminal, and by further performing flash Au plating. Au on the surface layer prevents the oxidation of Ni in the under-layer during storage, and when connecting a solder the Au diffuses into the solder rapidly, thereby fresh Ni is exposed, exhibiting very high wettability to a solder.

However, the solder used here is an Sn-Pb solder, namely containing lead. It has been pointed out that machinery and tools using Sn-Pb solder after discarded are deteriorated by rain and snow, and by weathering, and give rise to soil and drinking-water pollution attributed to Pb components, with serious effects on the environment. For this, it is necessary to make haste in quickly change to electronic parts connected with a lead-free solder containing no lead.

In the case of an electroless Ni plating coat, connection is made using Sn-Pb/Ni. However, almost no studies have been done as to the connecting property between a lead-free solder and electroless Ni plating, because the electroless Ni plating coat has a short history, thus little developing in the connecting property.

Other and further features and advantages of the invention will appear more fully from the following description, taken in connection with the accompanying

drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view of the electrode  
5 structure of a semiconductor in one embodiment according to the present invention.

Fig. 2 is a graph showing the relationship between the half-width of X-ray diffraction and the shear strength of an Sn-Ag solder ball.

10 Fig. 3 is a graph showing a change in the crystallinity of electroless Ni plating by heating.

Fig. 4 is a graph showing the relationship between the P content of a nickel plating solution and crystallinity.

15 Fig. 5(a) is a typical explanatory view showing a method of measuring shear strength, Fig. 5(b) is a typical explanatory view of a sample in which a destructive boundary at the time of destruction arises in the inside of a solder, and Fig. 5(c) is a typical explanatory view  
20 of a sample in which a destructive boundary at the time of destruction arises at a boundary between the Ni plating surface and the solder surface.

#### DISCLOSURE OF THE INVENTION

25 According to the present invention, the following

means are provided:

(1) A method of connecting (jointing) an electronic part, comprising:

forming an electroless nickel plating coat  
5 containing phosphorous on a substrate metal layer which constitutes a connecting terminal of an electronic part, and

carrying out connecting to the nickel plating coat through a lead-free solder,  
10 wherein a half-width of X-ray diffraction of a (111) plane of Ni crystal in the nickel plating coat is 5 degrees or less; and

(2) The method of connecting an electronic part according to the item (1), wherein the plating coat is formed using  
15 an electroless nickel plating solution containing 5.5 mass% or less of phosphorous.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The inventors of the present invention have made  
20 studies concerning the connection of electroless Ni plating forming a connecting terminal of an electronic part. As a result, we have found that the following problems arise when connecting a lead-free solder to the electroless Ni plating coat. These problems have been  
25 found to arise significantly in the case of pads 300 $\mu$ m or less in size on wafer surface, CSP (chip size package),

and the like.

1. The adhesive strength is decreased more conspicuously in the case of a lead-free solder than in the case of an Sn-Pb solder.

5 2. Electroless Ni plating is eluted into a solder after repeating reflow.

3. Surface oxidation is easily caused when plating a gold thin film.

This brings about the results that the reliability  
10 of the connected section is conspicuously impaired. Thus, the inventors have made earnest studies to eliminate these drawbacks.

As a result, the present inventors have found the following fact. Specifically, diffusion between a solder  
15 and Ni metal takes place at the boundary between an Ni plating layer and the lead-free solder, to produce a diffusion layer of "electroless Ni plating/solder". The inventors have paid attention to the relations between this diffused layer and adhesion and between the diffused  
20 layer and crystallinity of the Ni plating layer. As a result, the inventors have found that the connection boundary between the solder/the electroless Ni plating can be improved by controlling the crystallinity of the electroless Ni plating, and also confirmed that this has a  
25 significant effect on the adhesion, to complete the

present invention.

The present invention will be explained in more detail below.

A method of connecting to a nickel coat of a semiconductor chip through a solder, in one embodiment of the present invention, will be explained, with reference to Fig. 1. An electrode substrate 3 made of Al, Cu or the like is formed on a semiconductor substrate 4 of a semiconductor element. The reference letter 5 represents an insulating film made of a resin. Because an oxidized film is naturally generated on the electrode metal layer 3, an acid or an alkali is used as an etching solution to remove the naturally oxidized film formed on the surface after degreasing treatment is performed. Commercially available zincate-treating solution is used just after the etching solution is washed away, to substitute the surface layer formed on the electrode substrate 3 with Zn, thereby preventing the surface layer from being reoxidized. Thereafter, the semiconductor element is washed with pure water, and then it is soaked in a phosphorous-containing electroless Ni plating solution which is generally used and heated to about 50°C to 90°C, to form an Ni plating coat 1 only on the electrode substrate 3. After the Ni plating film is formed in a predetermined thickness of about 0.5 to 20 $\mu$ m, the plating solution is washed with

water, to form a flash Au plating layer only on the Ni plating coat 1.

Next, the semiconductor element is soaked in a vessel filled with a melt solder, to selectively form a  
5 solder layer 2 for the formation of a bump on the place where the flash Au layer plating film is present. The solder used at this time is preferably a solder, such as Sn-Ag, Sn, and Sn-Ag-Cu, and these solders are lead-free solders in consideration of the problems after they are  
10 dumped. The temperature in the solder vessel is preferably about 180 to 250°C.

Although the case of connecting a semiconductor chip is described as one embodiment, a lead-free solder layer may be also formed in the same manner as mentioned in the  
15 above, on a phosphorous-containing nickel plating coat, in the case of a ball grid array in a package of electronic parts.

The present invention is to form an electroless Ni plating coat having high crystallinity of Ni in the  
20 phosphorous-containing electroless Ni plating coat to be formed at this time.

When a solder ball is placed on the Ni plating coat, diffusion takes place between the solder and the Ni metal at the phase boundary between the Ni plating coat and the  
25 solder, to produce an electroless Ni plating/solder

diffusion layer. It has been found that at this time, the adhesive strength of an Ni plating coat having high crystallinity improves by the generation of the highly-uniform diffused layer, thereby preventing the dissolution  
5 of Ni plating.

The crystal structure of Ni of a metal plating layer formed in a usual electroless Ni plating process differs depending on the type of plating solution to be used, a heat load in a plating step, or the like. The X-ray  
10 diffraction half-width of the (111) plane of Ni crystal was generally 6 to 12 degrees.

Therefore, electroless Ni plating coats changed variously in crystallinity were formed on a pad which was 80 $\mu$ m by 80 $\mu$ m square, and a lead-free Sn-Ag solder ball  
15 having a diameter of 150 $\mu$ m was placed thereon, to measure shear strength. The crystallinity of the electroless Ni plating coat is expressed by the X-ray diffraction half-width of the (111) plane in an X-ray diffraction analysis. The shear strength (adhesive strength) shows the force  
20 required to peel off a solder from a plating coat. The obtained results are shown in Fig. 2.

It is understood from these results that the shear strength is increased suddenly when the X-ray diffraction half-width of the (111) plane of Ni crystal is below 5  
25 degrees and the crystallinity is increased. As to the



solubility of an Ni plating coat in a solder, Ni is dissolved when the half-width is greater than 5 degrees whereas the dissolution of Ni can be prevented when the half-width becomes smaller than 5 degrees.

5           When the X-ray diffraction half-width becomes 5 degrees or less, a destructive boundary arises in the inside of the solder and no destruction arises at the boundary between the plating and the solder. No dissolution of the Ni plating is observed from the  
10 microphotograph of the boundary, and the diffused layer is formed uniformly.

          Although the adhesive strength can be secured and the elution of the Ni plating coat can be prevented if the X-ray diffraction half-width of the (111) plane of Ni  
15 crystal is 5 degrees or less, the adhesive strength is further increased when the X-ray diffraction half-width is 4 degrees or less, which is hence preferable. However, making the half-width 2 degrees or less is accompanied by technical difficulties, for example, in the preparation of  
20 the electroless Ni plating solution and in an annealing step and is therefore economically unadvisable. Therefore the X-ray diffraction half-width of the (111) plane of Ni crystal is more preferably in a range from 4 degrees to 2 degrees.

25           The inventors have found that there is a method

using annealing in a plating step, as means for increasing the crystallinity of electroless Ni plating containing phosphorous.

The inventors have made studies concerning the  
5 relationship between the annealing temperature in the electroless Ni plating step and the crystallinity of the produced electroless Ni plating layer, to obtain the result as shown in the graph of Fig. 3 by experiments. As is understood from this graph, it has been recognized that  
10 the X-ray diffraction half-width of the (111) plane of Ni crystal is made to be 5 degrees or less and the crystallinity increases by annealing treatment carried out at a temperature of 150°C or more. Also it has been found that if the nickel plating coat is coated with a lead-free  
15 solder, the adhesion of the coating improves and the dissolution of Ni can be prevented.

The annealing temperature is preferably 150°C or more. However, an Ni plating coat having a half-width of 4 degrees to 2 degrees is preferable in consideration of  
20 the adhesion to the solder, as mentioned above. Therefore the annealing temperature is more preferably 250°C to 400°C.

Also, the inventors have found a method in which the content of P in an electroless Ni plating solution to be  
25 used is controlled, as means for increasing the

crystallinity of the electroless Ni plating.

The inventors have made studies concerning the relationship between the content of P in the phosphorous-containing electroless Ni plating solution to be used and the crystallinity of the produced electroless Ni plating coat. As a result, we have obtained the results as shown by the graph of Fig. 4, by experiments, in the same manner as mentioned in the above. As is understood from this graph, it has been recognized that when the content of P in the electroless Ni plating solution drops below 5.5 mass%, the X-ray diffraction half-width of the (111) plane of Ni crystal of the electroless Ni plating coat is decreased to 5 degrees or less, thereby the crystallinity increases. If so, it is understood that when a solder is placed on the plating layer, the adhesion therebetween is improved and Ni can be thereby prevented from dissolving.

Accordingly, the content of P in the electroless Ni plating solution is preferably 5.5 mass% or less. As mentioned above also, the content of P is more preferably 4.5 mass% or less, in view of preferable adhesion to the lead-free solder.

From this point of view, it is clear that if the X-ray diffraction half-width of the (111) plane of Ni crystal of the electroless Ni coating is made 5 degrees or less by controlling the annealing temperature in the

plating step or the content of P in the plating solution, the adhesion to a lead-free solder can be secured and the dissolution of Ni is therefore prevented.

In the present invention, the shear strength is the  
5 force required to peel off the lead-free solder placed on the plating coat from the plating coat. A method of measuring the force is shown in Fig. 5(a) by way of a typical view. Fig. 5(b) is a typical view of the state in the case where a destructive boundary at the time of  
10 destruction arises inside of the solder. In the case of such a destructive state, the adhesion at the boundary was judged to be good. Further, Fig. 5(c) is a typical view of the state in the case where a destructive boundary at the time of destruction arises at a boundary between the  
15 Ni plating surface and the surface of a solder. In the case of such a destructive state, the adhesion at the boundary was judged to be poor.

The method for connecting electronic parts according to the present invention is characterized in that the X-  
20 ray diffraction half-width of the (111) plane of Ni crystal of the nickel plating coat is 5 degrees or less. This method, therefore, ensures good adhesion between the Ni plating surface and the surface of the lead-free solder, and it ensures very strong shear strength, and in this  
25 method, even if destruction arises, the destruction takes

place in the inside of the solder. Further, the  
electroless Ni plating is not eluted even by repeating  
reflow. In particular, even if a pad as small as 300 $\mu$ m or  
less is used, this effect can be sufficiently exhibited.  
5 Therefore, the reliability of the connecting portion is  
greatly improved.

Also, since the electronic part according to the  
present invention is one obtained by coating a nickel  
plating coat with a lead-free solder, it is free from a  
10 need to worry about environmental pollution even if  
electronic machinery and tools mounted with this  
electronic part is discarded as a waste.

#### EXAMPLES

15 The present invention will be described in more  
detail based on examples given below, but the present  
invention is not limited by these examples.

Example 1 Production of UBM (underlaid bump metal  
layer) using phosphorous-containing electroless nickel  
20 plating

A wafer having the following Al pad which is an  
electrode substrate was prepared.

Al pad on the wafer

Material: Al containing 1 mass% of Si

25 Size: 100 x 100 $\mu$ m

Thickness of Al: 1.0 $\mu$ m

Electroless Ni plating-Au plating was carried out on the pad of this electrode substrate in the following steps.

First, the pad is subjected to degreasing treatment  
5 performed at 21°C for one minute by using a degreaser  
having surface active ability, and the oxide film produced  
on the surface of the Al electrode was removed using an  
aqueous 3% hydrogen fluoride solution. Next, just after  
the resulted surface was washed away with a nitric acid  
10 solution, the electrode surface was treated using a  
commercially available alkali zincate solution (SABSTAR ZN  
111 (trade name), manufactured by Okuno Seiyaku) at 21°C  
for 2 minutes to substitute with Zn, thereby preventing  
the surface from being oxidized. In succession, after the  
15 zincate solution was washed away with pure water, the  
wafer was soaked in a commercially available medium-  
phosphorous-type electroless Ni plating solution  
(Electroless Ni Plating Nikoron Z (trade name),  
manufactured by Okuno Seiyaku) kept at 85°C for 30 minutes,  
20 to form an Ni plating coat on the Al pad. The thickness  
of the resulting film was 8.0 $\mu$ m. After the wafer was  
washed with pure water, an electroless Au plating solution  
(TKK-51 (trade name), manufactured by C. Uyemura & Co.,  
Ltd.) was used, to form a flash Au plating layer, at 85°C  
25 for 8 minutes. After washed, the wafer was subjected to

annealing carried out at 300°C for one hour.

The electroless Ni plating and annealing, performed in the above steps, brought about the result that the electroless Ni plating coat had a crystal structure in which the X-ray diffraction half-width of the (111) plane was changed from 5.5 degrees to 3.2 degrees.

The results of an investigation, made on adhesion and diffusion to an Sn-Ag solder as to whether annealing was performed or not, are shown below.

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Table 1 Comparison of conditions of shear strength and diffusion as to whether annealing was performed or not

	Shear test result		Condition of diffusion
	Shear strength/gf	Destructive boundary	
Annealing was not performed	40 gf	Destroyed at the Ni/solder boundary	Ni plating was dissolved into the solder and the diffused layer was scattered into the inside of the solder
Annealing was performed	70 gf	Destroyed inside of the solder	Ni plating was not dissolved into the solder and the diffused layer was formed uniformly

In the above manner, the crystal structure of the Ni plating coat was changed by the annealing, which improved the adhesion to an Sn-Ag solder and also the condition of

diffusion.

Example 2      Use of a P-containing electroless Ni plating solution having a P content of 4%

Electroless Ni-Au plating was carried out on the  
5 following pad which was an electrode substrate.

Pad

Pad surface: electrolytic copper

Pad size:  $\phi 300\mu\text{m}$  (shape of the pad: circular type)

10      Periphery of the pad: solder resist (epoxy)

Nickel plating was performed on the pad in the following manner.

First, the pad was subjected to degreasing treatment performed using a degreasing solution having surface  
15 active ability at 60°C for 5 minutes, and it was treated for one minute by using an etching solution composed of hydrogen peroxide/sulfuric acid, to remove the oxide film produced on the surface thereof. In succession, the pad was washed with 3% sulfuric acid for 30 seconds, and it  
20 was subjected to a catalyst solution treatment using a commercially available Pd catalytic solution having a Pd concentration of 3 mg/l for 2 minutes at 30°C, to impart the catalyst nucleus of Pd to the surface. Next, the pad was soaked in a solution having phosphorous content of 4%,  
25 which was obtained by adjusting a commercially available



electroless Ni plating solution (Electroless Ni Plating Nikoron Z (trade name), manufactured by Okuno Seiyaku) to pH 5.5, at 85°C for 30 minutes, to form an Ni plating coat on the pad. The thickness of the resulting film was 8.0 $\mu$ m.  
5 After the pad was washed with pure water, an electroless Au plating solution (TKK-51, manufactured by C. Uyemura & Co., Ltd.) was used, to form a Au plating layer, at 85°C for 8 minutes.

When this electroless Ni plating solution having a P  
10 content of 4% was used, the X-ray diffraction half-width of the (111) plane of Ni crystal of the resulting plating coat was 4.5 degrees.

An Sn-Ag solder ball was placed on the pad of the electroless Ni plating produced by this process, to carry  
15 out a shear test. As a result, it was found that all destructive phenomena occurred in the inside of the solder.

#### INDUSTRIAL APPLICABILITY

According to the method for connecting electronic  
20 parts according to the present invention, good adhesion between the Ni plating surface and the surface of a lead-free solder is obtained, very strong shear strength is obtained, and, even if destruction is produced, the destruction arises inside of the solder. Also, even if  
25 reflow is repeated, electroless Ni plating is not eluted.

In particular, even if a pad has a size as small as 300 $\mu$ m or less, this effect is sufficiently exhibited. Therefore, this method is preferably as a method to largely increase the reliability of the connecting portion.

5           Further, since the electronic part according to the present invention is produced by coating a nickel plating coat with a lead-free solder, the method of the present invention is preferable as a method free from a need to worry about environmental pollution even if electronic  
10 machinery and tools mounted with this electronic part is discarded as a waste.

          Having described our invention as related to the  
15 present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.